

# UNITED STATES PATENT OFFICE

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## DICARBAMYLGUANIDINE SALTS

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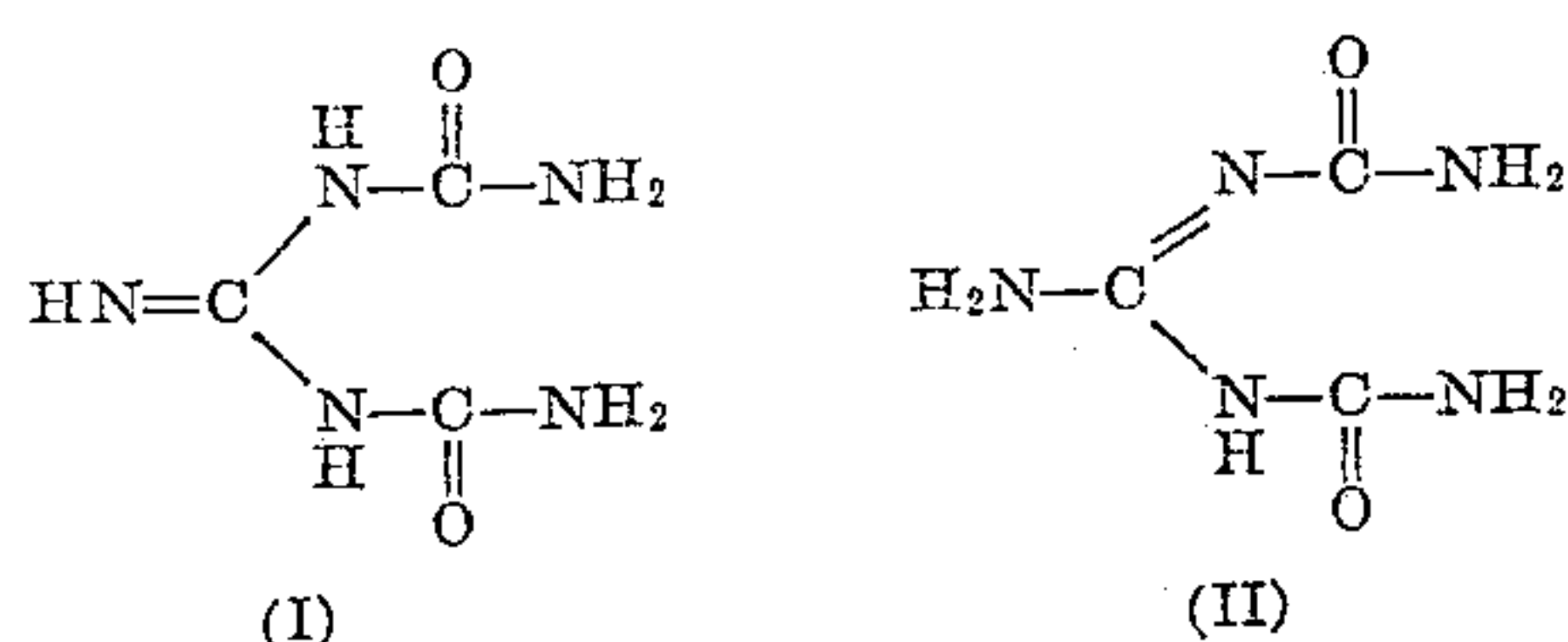
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6 Claims. (Cl. 260—553)

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The present invention relates to dicarbamylguanidine, a new compound, and its acid addition salts, and methods for their preparation.

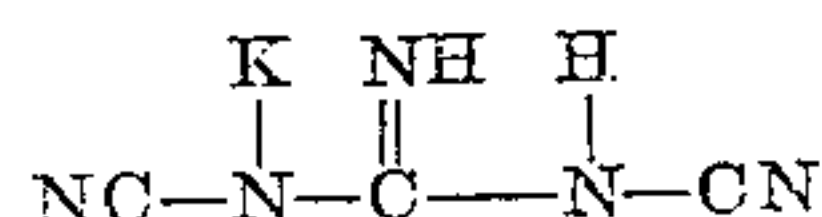
The structure of dicarbamylguanidine presents tautomeric possibilities, namely:



or I in equilibrium with II. Which of the three possibilities is the fact is not known. By "dicarbamylguanidine" therefrom is meant a member and/or equilibrium combination of the tautomeric system of I and II above.

The dicarbamylguanidines and their salts are useful in the preparation of synthetic resins, wetting agents, dyes, pharmaceuticals, and the like.

It is an object of this invention to prepare the dicarbamylguanidines by reacting a dicyanoguanidine, such as mono-potassium dicyanoguanidine, having the formula



(or a tautomer thereof) or the like, with a non-halogen acid in aqueous solution. Other objects will be apparent from the discussion of the invention following.

It was not to be expected that the cyano groups of the dicyanoguanidines could be hydrolyzed to the corresponding carbamyl groups in acid solution without cyclization in view of the fact that the potassium dicyanoguanidine reacts with hydrochloric acid, hydrobromic acid, and hydroiodic acid in aqueous solution to give the respective hydro-halide salts of ammeline.

It has now been found, however, that if instead of a halogen acid, a strong oxygenated acid such as sulfuric, nitric, phosphoric, p-toluenesulfonic, or the like, is used, the result is a dicarbamylguanidine salt instead of an ammeline salt. As used in the specification and claims, "strong acid" refers to an acid having an ionization constant of  $10^{-3}$  or greater.

The process is a general one for the dicyanoguanidines, and while dicyanoguanidine, free or containing organic substituents, may be used as such, it is preferred to liberate same in aqueous solution from one of their metal salts, as the free dicyanoguanidines when isolated are unstable. It is further preferred to use one of the alkali metal salts such as mono-potassium dicyanoguanidine, but any of the other salts, such

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as ammonium, zinc, calcium and the like, are suitable. The dicyanoguanidine salts, as well as the free compound, may be obtained by the process given in U. S. Patent 2,371,100.

In using a metal salt of a dicyanoguanidine it is necessary to add at least one mol of acid to combine with the metal in order to release the free dicyanoguanidine molecule, which then hydrolyzes to dicarbamylguanidine. However, better yields are obtained if a considerable excess of acid is used, excellent results being obtained when the acid:dicyanoguanidine ratio is about 5:1.

The following examples illustrate without limiting the invention.

### EXAMPLE 1

*The reaction of potassium dicyanoguanidine with nitric acid*

64 cc. of 70% nitric acid and 64 cc. of water were mixed in a 3-neck flask equipped with stirrer and thermometer. This solution was then heated on the steam bath and 14.7 g. of powdered potassium dicyanoguanidine was added slowly in the absence of applied heat over a 15 minute period. The flask was occasionally cooled in a water bath to keep the temperature below 100° C. The flask was then replaced on the steam bath and heated for 15 minutes. It was then cooled to 10° C. to render the crystals of dicarbamylguanidine mononitrate less soluble and the solution was filtered. The crystals obtained were rinsed with acetone, giving 21 g. of a pure product decomposing at a temperature greater than 360° C.

### EXAMPLE 2

*Preparation of dicarbamylguanidine*

Dicarbamylguanidine may be prepared by neutralizing any of its acid addition salts by a procedure analogous to the following.

Dicarbamylguanidine nitrate (62.4 g., 0.3 mol) was suspended in 350 cc. of water. 12.3 g. of sodium hydroxide dissolved in 100 cc. of water was added thereto and the mixture was heated to just boiling, whereupon a substantially clear neutral solution was obtained. The solution was cooled and the crystals filtered to provide 37 g. of dicarbamylguanidine melting at 176° C.

### EXAMPLE 3

*The reaction of potassium dicyanoguanidine with sulfuric acid*

A solution containing 100 g. of potassium dicyanoguanidine in 300 cc. of water was added to a solution of 300 g. of 95% sulfuric acid in 200 cc.



$$(\text{H}_2\text{N}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\overset{\text{H}}{\mid}}{\text{N}}-\overset{\overset{\text{NH}}{\parallel}}{\text{C}}-\overset{\overset{\text{H}}{\mid}}{\text{N}}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{NH}_2)_2 \cdot \text{H}_2\text{S O}_4 \cdot 2\text{H}_2\text{O}$$

### EXAMPLE 4

### EXAMPLE 5

### EXAMPLE 6

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$$\left[ \begin{array}{c} \text{H} \\ \text{C}_6\text{H}_{11}-\text{N}-\text{C}=\text{N}-\overset{\text{O}}{\parallel}-\text{NH}_2 \\ \text{N}-\text{C}-\text{NH}_2 \\ \text{H} \parallel \text{O} \end{array} \right]_2 \cdot \text{H}_2\text{SO}_4$$

Slotta et al., "Ber. deut. Chem.," vol. 63 (1930), pp. 208, 221 and 222.